III.A.8 Continuous Process for Producing Low-Cost, High-Quality YSZ Powder

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Objectives

- Develop a robust process for producing yttrium-stabilized zirconia (YSZ) powder that can be tailored to meet the Solid State Energy Conversion Alliance (SECA) Industry Team needs.
- Produce YSZ powder in 5-10 kg batches, and demonstrate reproducibility of the process.
- Demonstrate the advantages of tailoring YSZ powder characteristics to specific requirements of fabrication processes used in solid oxide fuel cell (SOFC) manufacture.
- Demonstrate that the process provides YSZ powder at low manufacturing cost.

Approach

- Use chemical precipitation methods to produce hydroxide precursors that can be converted into crystalline YSZ via thermal treatments.
- Use ball milling and attrition milling methods to reduce particle size of YSZ powders to below one micron.
- Use uniaxial and isostatic pressing methods followed by sintering to produce ceramic samples for density and ionic conductivity measurements.

Accomplishments

- Established a homogeneous precipitation process for preparing an yttrium-zirconium hydrous oxide precursor, which can be converted to crystalline YSZ via calcination.
- Established calcination and milling methods to prepare YSZ powders with controlled surface area and particle size distribution.
- Demonstrated that YSZ powder produced by the process can be sintered to densities greater than 98 percent theoretical at temperatures less than 1400ºC.
- Demonstrated sintered YSZ ceramics with high ionic conductivity (>0.08 S/cm at 800ºC), equivalent to the best values reported in the literature.
- Demonstrated that the manufactured cost of YSZ powder produced using the process will be less than $25 per kilogram at large production volumes.

Future Directions

- Continued process refinements aimed at increasing performance and reducing manufacturing cost. The emphasis of these studies will be on higher-cost unit operations, improving low-temperature sintering capability, and demonstrating process reproducibility.
- Demonstration of advantages of using tailored YSZ powders in fabrication processes used for the manufacture of SOFCs. This will involve fabrication of planar SOFC components using tailored YSZ powder and testing of the performance of these components.

- Production of evaluation samples of YSZ electrolyte powder, NiO/YSZ anode powder, and/or SOFC components produced from these powders for evaluation by SECA Industry Teams and Core Technology Program participants.
- Continual updates to the manufacturing cost analyses, incorporating process refinements that are implemented.

Introduction

One of the current barriers to reducing the manufacturing cost of SOFCs is the high cost of some of the critical raw materials. The availability of a low-cost, highly reliable and reproducible supply of engineered raw materials is needed to assure successful commercialization of SOFC technology. The yttrium-stabilized zirconia (YSZ) electrolyte material is a primary ingredient for two of the three layers comprising an SOFC element: the dense electrolyte layer and the porous nickel-based cermet (Ni/YSZ) anode layer. In addition, YSZ often is used as a performance-enhancing additive to lanthanum strontium manganite (LSM)-based cathode layers. In practice, the same YSZ raw material is used for each of the component layers, even though different fabrication processes are used for each layer. Significant opportunities for performance optimization and cost reduction would be possible if the YSZ raw material were tailored for each component layer. The project focuses on the development of YSZ powder synthesis technology that is "tailored" to the process-specific needs of different SOFC designs being developed under DOE's Solid State Energy Conversion Alliance (SECA) program.

Approach

NexTech's approach to developing a low-cost YSZ electrolyte powder production process is based on the following principles: (1) the process must be scaleable to high volume (500 tons per year) production at a cost of less than $25/kilogram; (2) the process must be sufficiently versatile so that powder characteristics can be tailored to a specific customer's requirements; (3) the process must be reliable, providing consistent batch-to-batch quality; and (4) the process must provide a relatively pure YSZ powder that meets performance criteria relative to particle size, surface area, sintering activity, and ionic conductivity. The process being developed in this project is based on homogeneous precipitation (see Figure 1). With homogeneous precipitation, the pH and solids content remain constant throughout the process, which is the key to achieving uniformity and reproducibility of the finished product. Another attribute of the homogeneous precipitation process is that it can be made continuous with constant replenishment of the feed solutions. This provides considerable cost and reliability advantages relative to current chemical synthesis processes.

In the project, synthesis studies are being conducted to identify optimum precipitation conditions for producing hydrous oxide precursors. These precursors then are processed into YSZ powders by washing and drying of the precipitates, calcination of the dried precursor to form a crystalline YSZ powder with targeted surface area (~10 m^2/gram), and milling of the calcined YSZ powder to sub-micron particle size. The YSZ powders are subjected to a comprehensive characterization protocol involving x-ray diffraction, chemical analyses, particle size distribution, surface area measurements, and sintering studies. Performance of sintered YSZ ceramics is being assessed by density measurements, ionic conductivity measurements, mechanical property measurements, and scanning electron microscopy.

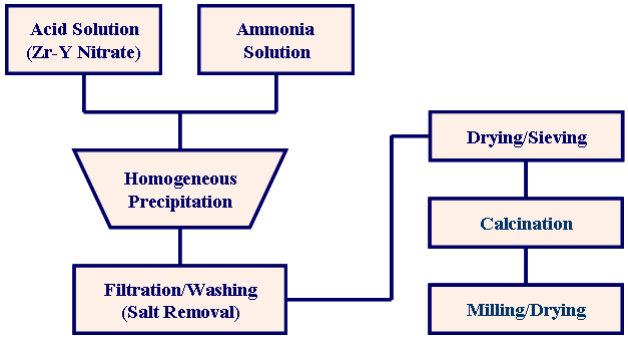

Figure 1. Homogenous Precipitation Process for YSZ Powder

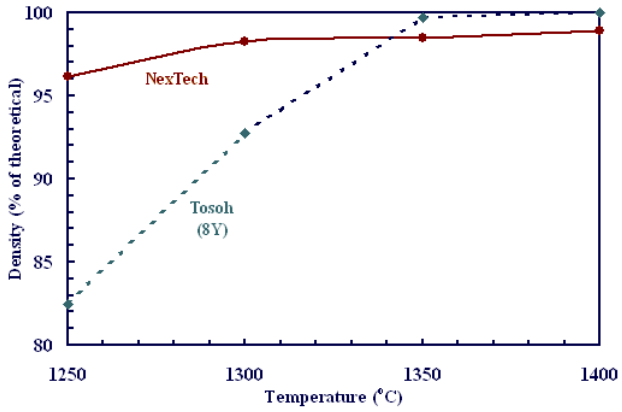

Figure 2. Sintering Performance of Experimental YSZ Powder, Compared to Commercially Available YSZ Powder

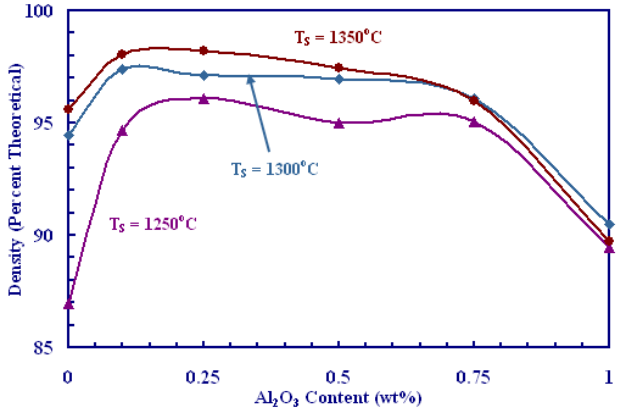

Figure 3. Effect of Al_2O_3 Content on Sintering Performance of Experimental YSZ Powder

Results to Date

In this project, NexTech has demonstrated a laboratory-scale continuous (homogeneous) precipitation process for YSZ electrolyte powder with equivalent, and in some ways superior, performance to YSZ powder that is commercially available from non-domestic suppliers. Key results to date are discussed below:

- The initial precipitation conditions were shown to have a profound effect on the performance of fully processed (calcined and milled) YSZ powders. After optimization of precipitation conditions, YSZ powders were produced that exhibited excellent low-temperature sintering performance compared to the current industry-standard YSZ powder (Tosoh 8Y). This is shown in Figure 2. Densities of >96 percent theoretical were achieved with a sintering temperature of 1250ºC, compared to a density of <82 percent theoretical for the commercial YSZ powder.
- NexTech also demonstrated improved densification through doping with alumina (Al_2O_3), nickel oxide (NiO) and manganese oxide (Mn_2O_3) dopants, especially at low sintering temperatures (less than 1300ºC). The optimum Al_2O_3 dopant concentration appears to be in the range of 0.25 to 0.50 weight percent, as shown in Figure 3.
- Ionic conductivities of sintered YSZ ceramics are essentially the same for ceramics derived from experimental and commercial YSZ powders (see Figure 4). Alumina dopants resulted in a slight reduction of conductivity, whereas NiO and Mn_2O_3 dopants resulted in more significant reductions of ionic conductivity.
- A manufacturing cost analysis confirmed that YSZ powder prepared by NexTech's homogeneous precipitation process could be manufactured at a cost of less than $25 per kilogram (see Figure 5). This analysis was based on a production volume of 500 metric tons per year, which is a fraction of the volume necessary when SOFCs are in full-scale production.

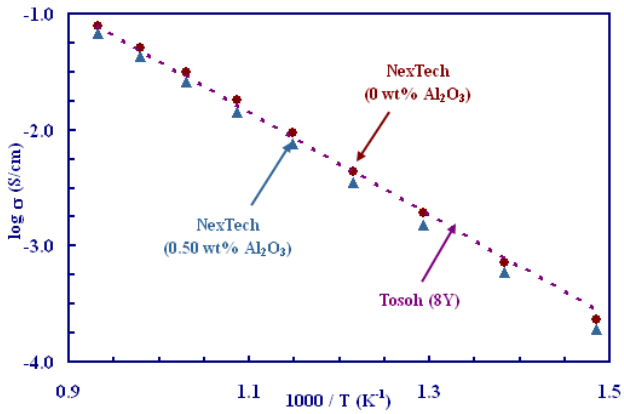

Figure 4. Ionic Conductivity Data for YSZ Ceramics

Conclusions

- Homogeneous precipitation is a promising route for the continuous synthesis of hydrous oxide

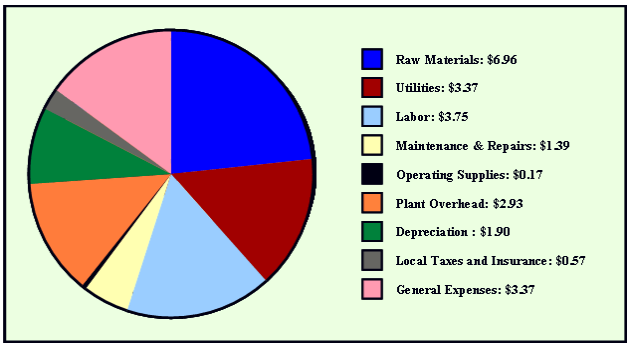

Figure 5. Results of Manufacturing Cost Analysis

precursors to high-quality YSZ powders. The initial precipitation conditions had a profound effect on downstream milling performance (after calcination) and on subsequent sintering and electrical performance. Important synthesis variables include concentrations of the precipitant solutions, feed rates during precipitation, and the pH during precipitation.

- The processing of the precipitated hydroxide slurries prior to drying was critically important to achieving high-performance YSZ powders. For aqueous processing, surfactants were required to allow hydroxide precipitates to be dried directly from aqueous suspensions. An alternative approach, based on solvent exchange of the precipitated hydroxides into isopropyl alcohol prior to drying, also was demonstrated.
- Several oxide dopant strategies were identified that led to significant improvements in sintering performance of YSZ ceramics. Dopants such as aluminum oxide, nickel oxide, and manganese oxide all were found to increase ceramic densities, especially with low sintering temperatures (~1200 to 1300ºC). These dopants also led to a reduction of ionic conductivity, which suggests a trade-off between dopant concentration, low-temperature sinterability, and ionic conductivity.
- Based on a manufacturing cost analysis, YSZ powders prepared by the homogeneous precipitation process can be manufactured at a cost of less than $25 per kilogram at high production volumes. This analysis identified specific unit operations where cost can be reduced upon further optimization.

FY 2004 Publications/Presentations

1. S.L. Swartz, et al., *Continuous Process for Low-Cost, High-Quality YSZ Powder*, SECA Annual Workshop and Core Technology Program Peer Review Workshop (May 12, 2004).

2. S.L. Swartz, et al., *Continuous Process for Low-Cost, High-Quality YSZ Powder*, SECA Core Technology Program Review Meeting (October 1, 2003).